Synthesis and Application of γ-Alumina Nanopowders

A Dissertation

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By

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CERTIFICATE

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This is to certify that the dissertation entitled "**Synthesis and Application of γ-Alumina Nanopowders"** being submitted by **Shuchismita Dey** to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bonafide research carried out by her under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

N.I.T. Rourkela**.**
Date:

Dr. Aparna Mondal
(Supervisor)

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Rourkela

Date: Shuchismita Dey

ABSTRACT:

Aluminum oxide (Al_2O_3) nanopowder was synthesized using $AlCl_3{\cdot}6H_2O$ as the starting material by the aqueous based precipitation method and applied in removal of Cr (VI) ion from aqueous solution. The characteristics of the sample were investigated by X-ray diffraction studies, DSC-TG analysis, and IR techniques. From the thermal studies the mass loss was found to be 45%. The study of the evolution of crystalline phases of obtained powders was accomplished through X-ray diffraction studies. XRD data showed that the sample calcined at 650°C has γ-Al_2O_3 phase. The crystallite size and particle size were rapidly changed over 1000°C and cause the formation of α-Al_2O_3 phase. FTIR results showed that the calcined nanoparticle were also free from surfactant. The prepared γ-Al_2O_3 nanopowders were applied for removal of Cr (VI) ions from aqueous solution. The effects of contact time on the extent of removal of Cr (VI) ions were also investigated. The results indicate that the prepared aluminum oxide via surfactant assisted route may have potential as novel, and effective adsorbent for removal of hexavalent chromium Cr(VI) ion from aqueous solution.

Chapter 1

INTRODUCTION

1.1. Aluminum oxide and its Application

Aluminium oxide is a compound of aluminium and oxygen with chemical formula of Al_2O_3. It is the most commonly occurring of several aluminium oxides, and specifically identified as aluminium (III) oxide. It is commonly called alumina. The oxides of aluminium materials are widely used in ceramics, refractories and abrasives due to their hardness, chemical inertness, high melting point, non-volatility and resistance to oxidation and corrosion [1-5]. The importance of alumina as catalyst or catalytic support has also been widely recognized for many chemical reactions [6-8]. The transparency of alumina film and wide range of properties extend its application in optics as well [9]. Al_2O_3 is an electrical insulator having high thermal conductivity. Corundum or α-aluminum oxide is the most commonly occurring crystalline form of aluminum oxide and its hardness make it suitable for applications as an abrasive and as a component in cutting tools.

Al_2O_3 powder has wide range of applications such as electronic ceramics, high strength materials and catalysts. Among the seven polymorphs of transition alumina identified so far, namely, phases γ, η, δ, θ, χ, κ, and ρ, the γ form is one of the most extensively used in industrial catalysis owing to its comparatively large surface area, unique surface characteristics, and exceptional structural stability. γ-alumina contains the same ratio of Al to O atoms as in α-alumina the only difference is that it has a tetragonal structure where there are 8 cation vacancies for every 160 atoms [10]. Conventional γ-alumina formed through the thermal dehydration of a crystalline aluminum oxyhydroxide (boehmite) at a temperature above 450°C. The γ-phase is a metastable phase and on heating it will form the thermodynamically stable α-phase. Recently many researchers are showing interest on the preparation and application of nano-sized alumina considering their diverse properties [11-15]. The property of such alumina particles are depends on particle size, morphology, surface and phase homogeneity and these properties can be controlled by selecting a proper synthetic route. γ-alumina with high surface properties such as high surface area and mesoporous properties is commonly used as a high temperature catalyst or catalytic support and as a membrane. A mixture of alumina phases (θ, δ and γ) are generally

obtained by sol-gel technique and on heating at high temperature these transform to a stable α-alumina phase. In our study, we have chosen aqueous based method which is simple and economic for the synthesis of pure alumina and modified alumina nanomaterials.

1.2. Literature Survey

Zhang and Pinnavaia [16] synthesized mesoporous γ-Al_2O_3 through surfactant mediated scaffolding of peptized pseudoboehmite nanoparticles. The surfactant was removed upon calcination of the resulting surfactant-containing composites at 500°C and concomitantly converts the pseudoboehmite crystallites to γ-alumina through topochemical transformation with the retention of the scaffold structure.

Baumann *et al.* [17] synthesized high surface alumina aerogels with low density (60-130 kg/m^3), high surface area (600-700 m^2/g) without the use of alkoxide precursors by the addition of propylene oxide to aqueous or ethanolic solution of hydrated aluminium salts, like $AlCl_3.6H_2O$ or $Al(NO_3)_3.9H_2O$ which was then dried by supercritical CO_2. XRD and TEM analysis indicated that the aerogels prepared from hydrated $AlCl_3$ in water or ethanol possessed microstructures which contain highly reticulated networks of pseudoboehmite fibres, 2-5 nm in diameters and varying length. Alumina aerogels was transformed to γ- Al_2O_3 on calcination at 800°C.

Lee *et al.* [18] synthesized unidirectional alumina without addition of organic solvent through hydrothermal route using a surfactant and an aluminum precursor (aluminum tri-*sec*-butoxide). Through this procedure unidirectional nanostructure such as nanotubes, nanofibers and nanorods were obtained depending on the nature of surfactant used. The materials maintained their γ-alumina phase up to the temperature of 1050°C.

1.3. Chromium ions, its advantage and disadvantage

Cr (VI) is one of the most toxic pollutants generated by the electroplating, metal finishing, leather tanning, photography, and dye and textile industries [19-22]. Cr exists both in trivalent Cr (III) and hexavalent Cr (VI) forms. Trivalent chromium is considered as a micronutrient for human, plant and animal metabolism. It is less toxic than hexavalent chromium which is extremely mobile in the environment and very toxic to living organism. The world Health organization (WHO) recommends the maximum allowable limit for the discharge of Cr

(VI) in surface water is 0.1 mg/L, and in drinking water is 0.05 mg/L. So, Cr (VI) should be removed from aqueous solution to avoid the deleterious impact of the Cr(VI) on the human health. There are various methods available for removal of hexavalent chromium from water such as chemical precipitation, adsorption and bio-sorption reverse osmosis, ion exchange, electrodialysis, and photo-catalysis. Adsorption method is one of the potential remedies to removal of the contaminants.

Objective of the present work

The main objectives of the present experiment are:-

- Synthesis of γ-Al_2O_3 through surfactant assisted route using inorganic precursors and a surfactant.
- Effect of calcination temperatures on phase transformations of Al_2O_3.
- Structural characterization using DSC-TG, XRD, and IR analysis.
- Application of the synthesized powders for removal of Cr(VI) ions from aqueous solutions.

Chapter 2

EXPERIMENTAL PROCEDURES

2.1 Materials

- Aluminum chloride hexahydrate ($AlCl_3.6H_20$)
- Ammonium hydroxide (NH_4OH)
- Potassium dichromate ($K_2Cr_2O_7$)
- Brij56 ($C_{16}H_{33}(-OCH_2CH_2)_{10}$ OH)

2.2. Method of Preparation

2.2.1. Preparation of aluminum oxide

Aluminum chloride hexahydrate ($AlCl_3.6H_2O$) was used as a starting material for the preparation of aluminum oxide. An aqueous solution of $Al_2Cl_3.6H_2O$ was prepared. The pH of the solution was controlled by adding drop wise NH_4OH as a precipitating agent and the solution was stirred continuously with a magnetic stirrer. Washing of the powder with distilled water and

filtration of the solution were performed and then ethanol was used to wash the powder for three to four times. The washed powder was dried and calcined for 2 h at 500, 600, and 1000^{o}C.

2.2.2. Preparation of aluminum oxide and brij-56 nanoparticles

Surfactant solution was prepared by adding brij56, acetone and isopropanol by continuously stirring and heating. After preparation of brij56 solution similar method was used for the preparation of aluminum oxide at the same pH. Both the solution was mixed by adding brij56 solution drop wise to $AlCl_3{\cdot}6H_2O$ solution and pH of the solution was maintained by adding NH_4OH drop wise. After preparation of sample same method has been used for washing and drying of sample. The experimental procedure is schematically shown in Fig. 3.1. The as-prepared and calcined powders were studied using different characterization techniques. Formation of γ-Al_2O_3 phase was verified by XRD analysis. The shape and morphology of particles were studied by SEM.

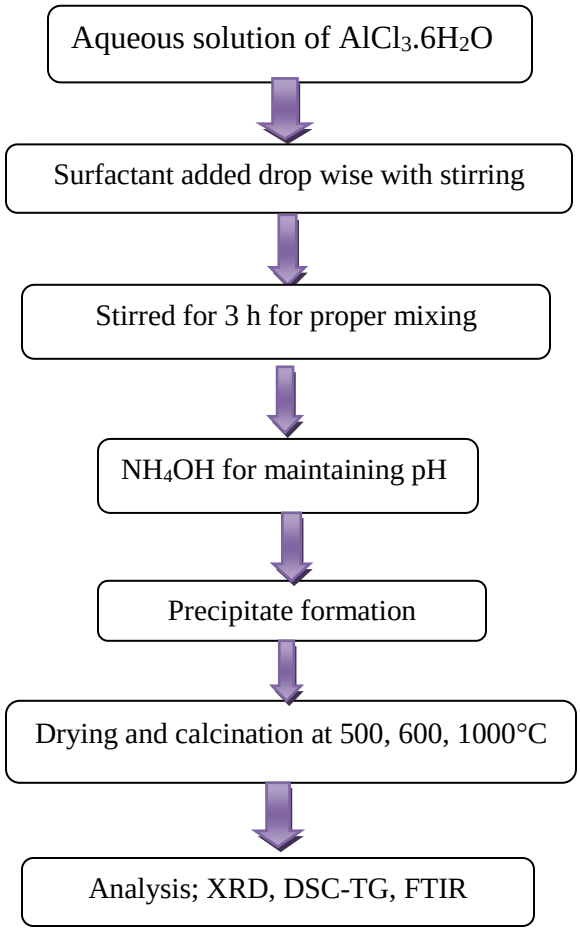

Fig 2.1. Schematic diagram of synthesis of Al_2O_3 powder using metal inorganic precursor.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Thermal analysis

The thermal decomposition features were followed using differential thermal analysis as well as thermo gravimetric analysis. TGA is a technique for measuring the changes in weight of a sample as a function of temperature and time. On heating, over 30 to 1000°C, the as prepared boehmite, which is the precursor for Al_2O_3 decomposes and burns out instantaneously, resulting in Al_2O_3 powder. The weight loss in the low temperature range was due to the removal of physisorbed water. Figure 3.1 shows the TGA curves of the as-prepared alumina precursor sample synthesized by adding surfactant. The TGA curve shows 14% weight loss in the temperature range of 33-150°C, due to desorption of physisorbed water molecules. A 5 % weight loss in the region of 150-235°C is attributed to the decomposition of the precursor and removal of chemisorbed water. About 33 % weight loss in the temperature range 235-500°C is due to the removal of organic groups and crystallization of Al_2O_3 and associated with a broad exothermic peak centered at 460°C.

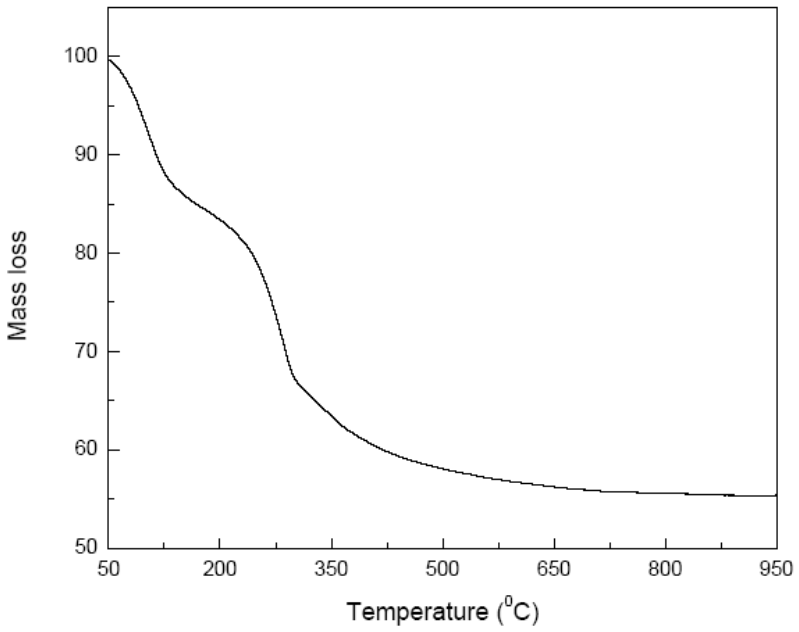

Fig. 3.1. TGA curve of as prepared alumina precursor synthesized using a surfactant.

3.2. XRD analysis

The determination of the crystalline phases was carried out by using X-ray diffraction (XRD) patterns which were obtained with Cu K radiation (λ = 1.5406 A^{O} and θ = 20-80) at room temperature. By using scherrer's equation the average crystallite size of obtained powders was estimated from XRD pattern. Figures 3.2 and 3.3 show the X-ray diffractograms of Al_2O_3 nanopowder synthesized with and without surfactant and then calcined at 500 and 650° for 2 h. All the peaks were indexed to γ-Al_2O_3 with strongest reflection at 2θ = 66.8°. Baumann *et al.* [17] also observed that the alumina aerogels was transformed to γ- Al_2O_3 on calcination at 800°C. As the calcined temperature increased to 1000°C, a phase transformation from γ- Al_2O_3 to mixed phases of Al_2O_3 occurred as can seen from Fig. 3.4. The surfactant here plays important role in decreasing the crystallite size as given in Table 3.1.

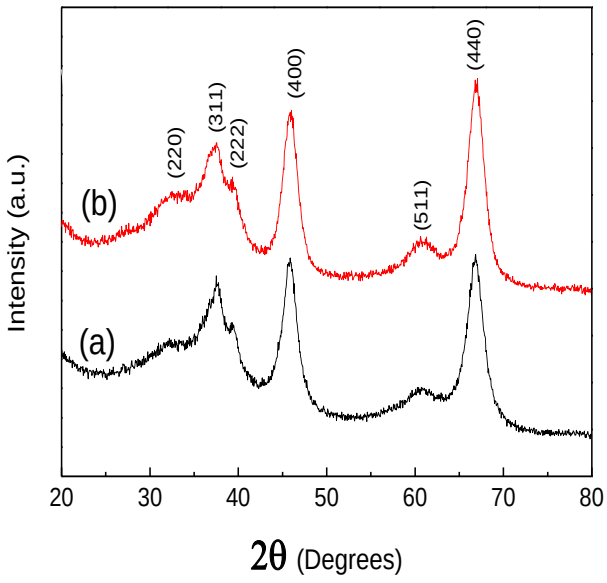

Fig. 3.2. X-ray diffractogram of Al_2O_3 nanopowder calcined at (a) 500 and (b) 650°C.

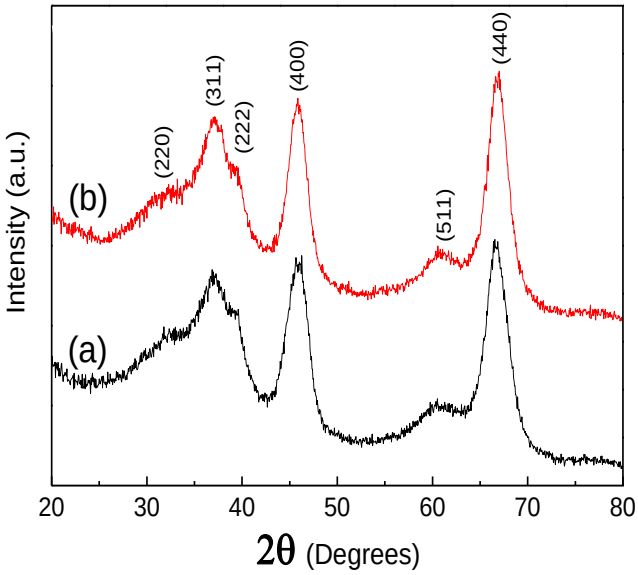

Fig. 3.3. X-ray diffractogram of Al_2O_3 nanopowder synthesized using brij and then calcined at (a) 500 and (b) 650°C.

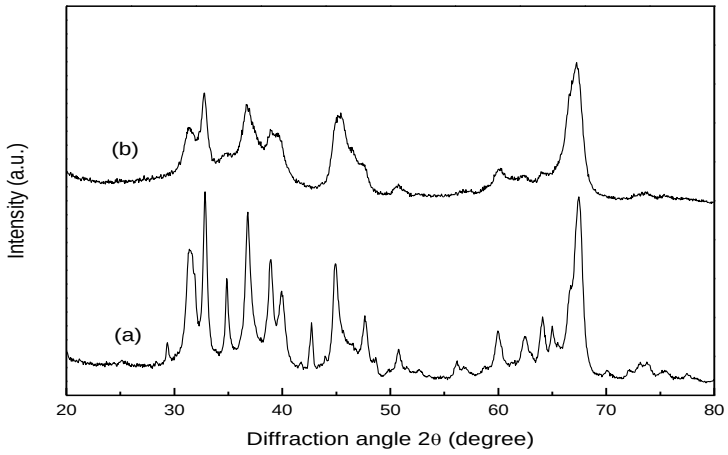

Fig. 3.4. X-ray diffractogram of Al_2O_3 nanopowder synthesized (a) without and (b) with brij and then calcined at 1000°C.

Table 3.1. d-spacing and crystallite size of Al_2O_3 powders calcined at different temperatures.

SAMPLE	d-spacing	Crystallite size (nm)
	Without surfactant	
Calcined at (°C)		
500	1.4003	6.8
650	1.4007	7.2
1000	1.3888	22.2
	With surfactant	
500	1.4017	5.3
650	1.3999	6.1
1000	1.3933	11.6

3.3. FTIR Analysis

The IR spectra of as-prepared and the calcined powders, synthesized with and without surfactant are shown in Fig. 3.5. The large band between 800 and 400 cm^{-1} due to Al-O-Al band. The stretching vibration of the Al-O-Al bond and broadening of this band is due to the distribution of vacancies among the octahedral and tetrahedral sites, leading to a spreading out of the Al –O vibration frequencies. In addition to alumina bands there are bands at the surface due to chemisorbed and adsorbed species. The large band centered at 3226-3480 cm^{-1} results from the superposition of vibration bands of bonded hydroxyl groups, isolated OH groups and stretching vibrations of adsorbed water molecules. The band 1554 cm^{-1} is due to bending of molecular water. The peak from 1731-1742 cm^{-1} is assigned to (C=O) stretching.

The IR spectra of (a) as-prepared sample synthesized with surfactant showed a broad peak at 3555 cm^{-1} corresponding to -OH stretch, and a sharp peak at 1650 cm^{-1} corresponding to -OH bend. The intense peaks at 1405 and 3150 cm^{-1} are characteristic bands of the surfactant. The band at 1050 cm^{-1} observed in the as-prepared sample is due to the vibration mode of -OH groups on the boehmite. On calcination at 500°C, there was a significant reduction in the

intensity of the -OH stretch. Almost no peak related to surfactant was observed indicating the removal surfactant.

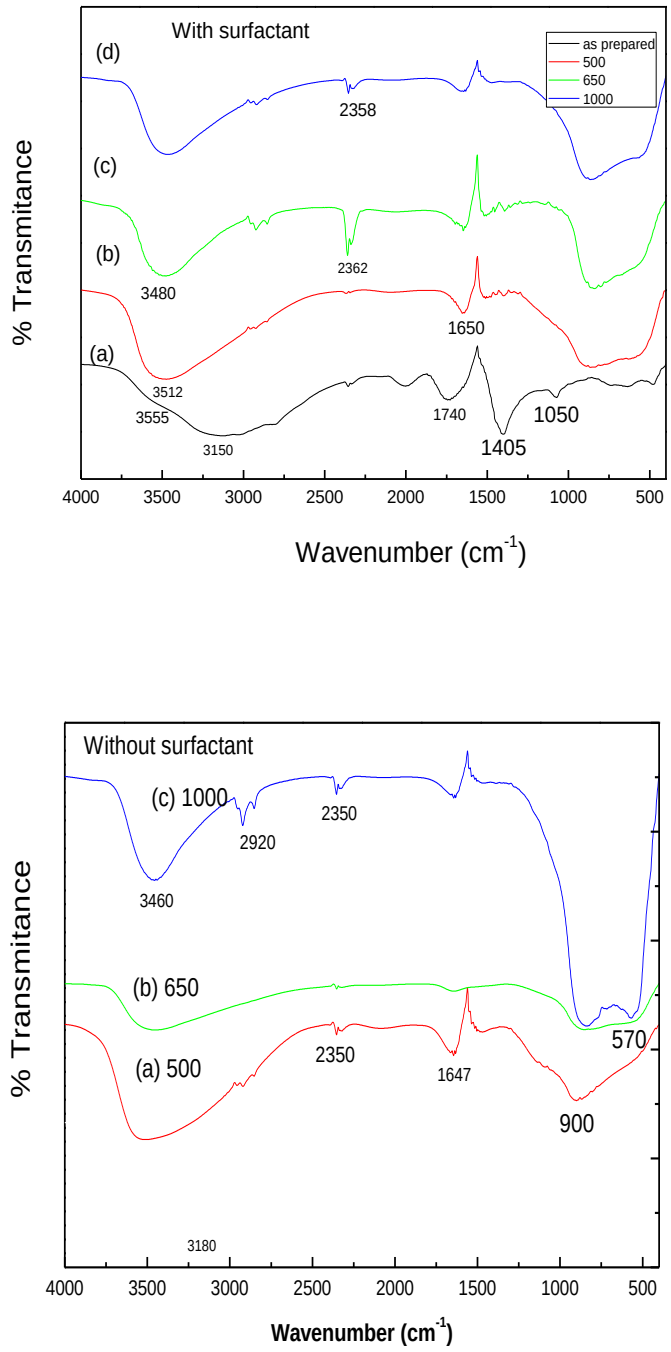

Fig. 3.5. FTIR spectra of Al_2O_3 nanopowder synthesized with and without brij and calcined at different temperatures.

APPLICATION

3.4. Removal of Cr (VI) from aqueous solution

A stock solution (500 ml) of $12x10^{-4}$ M concentration was prepared by dissolving the chromium dichromate (0.1764 gm) in distilled water. Then by dilution method different concentrations ($12x10^{-4}$ to $4x10^{-4}$ M) of stock solutions were prepared. Batch experiments were performed for same initial concentration ($8.5x10^{-4}$M) of Cr(VI) ion at different time interval in presence of 0.2 g of alumina-brij56 nanoparticle in 100 ml of solution for 2h. To $8.5x10^{-4}$(M) Cr (VI) solution, pure alumina with and without brij56 was added in two different beakers under stirring for 2 h. Regular sampling from the solution was done at noted time interval (15 min, 30 min, 45 min, 60 min, 90 min and 120 min) and was analyzed by UV-Visible spectroscopy.

Contact time is one of the most important parameters in adsorption process. It can be visualized from Fig. 3.6 that a rapid uptake of Cr (VI) ions takes place. Equilibrium was reached within 2 h of contact time. During initial stage of adsorption, there is a rapid uptake of metal ions which slowed down after 45 min of contact time. Initially a large number of vacant surface sites are available for adsorption which gets saturated gradually thereby increasing competition between adsorbate molecules for vacant surface sites. The adsorption efficiency depends on surface area of adsorbent.

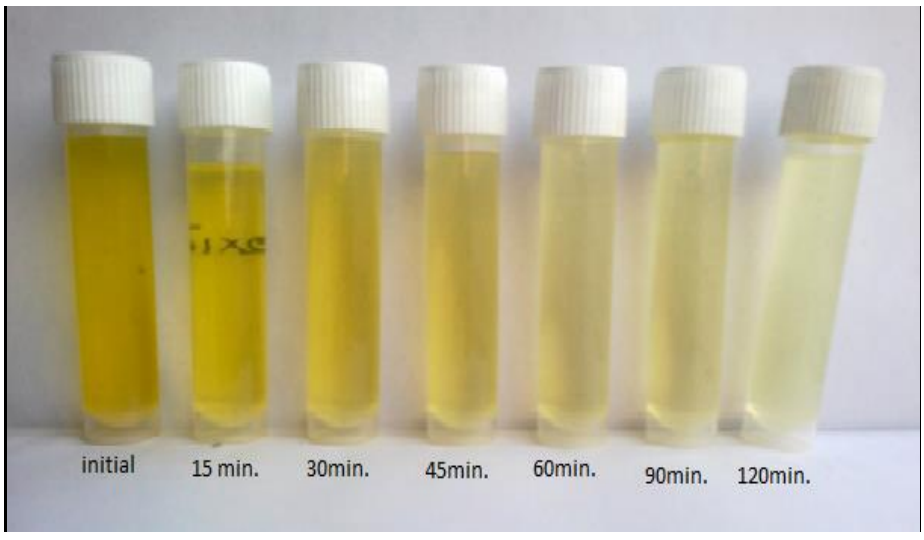

Fig. 3.6. Photographs of pure Cr(VI) solution (left) and solutions after different time intervals (from left to right) of adsorption by Al_2O_3 synthesized with surfactant.

The adsorption amount was calculated according to the equation:

% Removal = (A_o – A_t)/A_o *100

Where A_o = Initial concentration of Cr (VI), A_t = solution concentration at different time interval.

The synthesized Al_2O_3 nanoparticles were effective in removing the Cr (VI) ions within 120 min. The percentage of Cr(VI) removal after 120 min is 60.88 % with the capacity of 25.88 mg/g. The percentage of Cr(VI) removal after 120 min for pure aluminum oxide is 45.88 with the capacity of 20.18 mg/g. So, Al_2O_3 synthesized with surfactant is more effective in removing the Cr(VI) may be due to higher surface area.

CONCLUSION:

Al_2O_3 nanopowder was synthesized by surfactant assisted route using inorganic salts of aluminium chloride and brij as a surfactant. The prepared materials were characterized using various experimental techniques. The DSC curve shows small exothermic peak at 460°C due to phase transformation from amorphous to γ-Al_2O_3. FTIR results show that Al_2O_3 nanopowder heated at 500°C is almost free from surfactant. XRD results show that the as-prepared sample have boehmite phase while technologically important pure γ-Al_2O_3 phase was formed after calcination at 500°C temperature. The adsorption experimental revealed that aluminum oxide synthesized with surfactant is effective in Cr(VI) ion from aqueous solutions. Present work predicted that aluminium-brij56, as well Al_2O_3 as new kind of adsorbents, may have potential application in heavy metal ion removal from aqueous solution.

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